Minimum Energy Configurations of Repelling Particles in Two Dimensions

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Geometrical arrangements of minimum energy of a system of identical repelling particles in two dimensions are studied for different forms of the interaction potential. Stability conditions for the triangular structure are derived, and some potentials not satisfying them are discussed. It is shown that in addition to the triangular lattice, other structures may appear (some of them with non-trivial unit cells, and non-equivalent positions of the particles) even for simple choices of the interaction. The same qualitative behavior is expected in three dimensions.

I. INTRODUCTION

Nature teaches us that crystalline structures −namely, the periodic spatial arrangement of atoms− are the minimum energy configurations (MECs) of systems with a great number of particles (at least in the case where these particles come in only a small number of different types). The determination from first principles of the most stable crystalline structure of a substance, given the properties of its constituent atoms and their interactions is a complicated minimization problem for which exact methods do not exist. A usual way of determining the MECs is to compare the energy of different proposed structures, and pick up the lowest energy one. The numerical simulation of finite systems, using the technique of simulated annealing may be of great help in this process, since if the cooling down of the system is sufficiently slow during the simulation, then we expect that the particles accommodate to its MEC.

When all particles in the system are identical and may be considered as point-like, interacting through a potential energy that depends only on their relative positions, the problem simplifies greatly. In real pure materials, most of the MECs correspond to the high symmetry structures hcp, bcc, fcc, and sc. Other structures (notoriously the phases of carbon and ice) are largely due to the directionality of atomic orbitals. We will concentrate here in the case of isotropic interactions. It is known that even in this case, a rather complicated radial interaction potential $U(r)$ (for instance, an oscillating potential) may give rise to complex structures (quasicrystals, for instance).[1] If we restrict to the case of repelling interactions ($U'(r) \leq 0$), with only an external pressure preventing the particles to move away from each other, the MECs seem to be limited to the above mentioned hcp, bcc, fcc, and sc structures. In the case of particles in two dimensions, and under the conditions that all particles are identical and the interactions are repulsive, the general believe is that the triangular structure (TS) is always the MEC (I will use 'triangular' since it is the most commonly used term, although from symmetry consider-

ations the word 'hexagonal' would be more appropriate).

The aim of this work is to analyze the possible existence of structures other than the triangular, for identical particles interacting in two dimensions. The case of power-law, cut-off power-law, and potentials with a hard-core plus a soft repulsive shoulder are discussed in detail. It will be shown that the TS may not be the MEC even for some 'simple' forms of $U(r)$.

The paper is organized as follows. In the next section the local stability of the TS against a displacement of a single particle is discussed. The MECs of a family of potentials that does not satisfy this criterium are shown in Section III. In Section IV, a stability criterium against a global deformation is derived, and some potentials that do not satisfy it are identified. Finally, in Section IV there is a short summary and some discussion about topics that are not deeply considered in the paper, namely the case of three dimensional systems, the effect of temperature and other dynamical effects.

II. LOCAL STABILITY OF THE TRIANGULAR STRUCTURE

We will consider a system of identical particles lying on the plane, and interacting through a two-body repulsive spherical potential $U(r)$, $U'(r) \leq 0$, where r is the separation between particles. The system is supposed to be constrained by an external pressure P. We will try to find the geometrical configuration of the particles that minimizes the free energy of the system. The MEC must be obtained by minimizing the enthalpy $H = E + PV$, where V is the volume, and the energy E is given by

$$E = \frac{1}{2} \sum_{\mathbf{r}_i \neq \mathbf{r}_j} U(|\mathbf{r}_i - \mathbf{r}_j|). \tag{1}$$

The complete solution of this problem by analytical means is out of our possibilities. But since the TS is our initial guess to the MEC, we can start by analyzing its *local* stability.

Clearly, if the TS is the MEC, the energy of the system must increase when a single particle is slightly displaced from its lattice position. The potential around a given site (taken to be the origin of coordinates) created by a particle at a generic position $\mathbf{r}_0$ is, up to second order, of the form $U''(r_0)\,\delta x^2 + \frac{U'(r_0)}{r_0}\delta y^2 + U'(r_0)\,\delta x + U(r_0)$, where δx (δy) is the coordinate of the tested point measured along (perpendicular to) $\mathbf{r}_0$. This potential must be summed up for all particles, and for lattices with rotational symmetry C_3 or higher (as it is the case for the TS) it must reduce to a isotropic form. Considering the invariance of the trace of cuadratic forms under rotations, the cuadratic part of the final effective potential can be written as $U_2\left(\delta r/a\right)^2/2$, with

$$U_2 = a^2 \sum_{\mathbf{r}_i \neq 0} \left[U''(r_i) + \frac{U'(r_i)}{r_i} \right], \qquad (2)$$

where the sum is over all particles of the lattice. The introduced parameter a is arbitrary, but it will be taken to be the lattice parameter of the TS, in such a way that U_2 can be directly compared for lattices with different lattice parameters. The positiveness of U_2 is the condition for the stability of the lattice under small displacements of a single particle.[2]
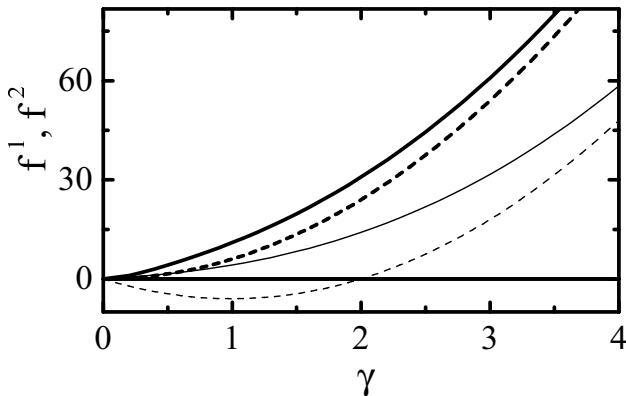

FIG. 1. The functions $f^1(\gamma)$ (thick lines) and $f^2(\gamma)$ (thin lines) to be used for the calculation of the rigidity of the triangular lattice against the displacement of a single particle and a global rescaling (see text). Dashed lines are the contribution of nearest neighbors only.

Let us consider some particular cases. For $U(r) = U_0\left(r_0/r\right)^\gamma$ all terms of the sum in (2) are positive and the sum is convergent for all $\gamma > 0$. The value of U_2 is given by

$$U_2 = f_1(\gamma)\,U_0\left(r_0/a\right)^\gamma, \qquad (3)$$

with the adimensional function $f_1(\gamma)$ given by

$$f_1(\gamma) = \gamma^2 \sum_{\mathbf{r}_i \neq 0} \left(r_i/a\right)^{-\gamma-2}. \qquad (4)$$

The function $f_1(\gamma)$ is plotted in Fig. 1. In this figure, the contribution to f_1 coming only from nearest neighbors is also shown, and it is clear that the contribution of particles at larger distances becomes more relevant as γ goes to zero. We note in addition that U_2 vanishes for $\gamma \to 0$. This is related to the fact that $\gamma \to 0$ gives a logarithmic interaction between particles ($\lim_{\gamma \to 0^+} \frac{x^{-\gamma}-1}{\gamma} = -\ln(x)$), that corresponds to two-dimensional charges, and it is well known that the equilibrium configuration in this case has all charges at the borders of the system, so no TS is stable in this case.

Now we will turn to cases when U_2 can be negative. First of all we should notice that (2) is proportional to the Laplacian of $U(\mathbf{r})$, namely

$$U_2 = a^2 \sum_{\mathbf{r}_1 \neq 0} \Delta U(\mathbf{r}_i). \qquad (5)$$

so the problem has an electrostatic analog. Considering the electrostatic problem $\Delta U = -\rho$, if we look for potentials $U(r)$ such that $\Delta U \leq 0$ for all r, we need a positive (or zero) charge density ρ at all distances. But if in addition we require that $U(r)$ vanishes sufficiently rapid for $r \to \infty$, we are forced to locate a negative charge at the origin (of the same absolute value than the integrated positive charge). This choice produces a potential $U(r)$ that goes to $-\infty$ at the origin, i.e., it would not be repulsive at short distances. This shows that U_2 cannot be negative at all distances for repulsive short range interactions. However, since expression (2) must be summed up only over a discrete set of values to test for stability, we can get a negative value of U_2 with different simple elections. One way is choosing a linear function $U(r) \sim \alpha - \beta r$ $(\beta > 0)$. In order to get a reasonable potential we have to cut it off at large distances. Beyond $r = r_1 \equiv \alpha/\beta$ the potential would be taken as zero, and for $r < r_0$ $(< r_1)$ a strong hard-core will be supposed to avoid a complete collapse of the particles. This interaction will be referred to as the hard-core plus linear-ramp potential.[3] For this potential, U_2 is negative as long as there is no particles at distances r_0 or r_1 from each other. In particular, if we restrict to values of r_1 and r_0 such that $r_1/r_0 < \sqrt{3}$, we can conclude that a TS with lattice parameter a, with $r_0 < a < r_1$ is unstable. The question is, what is the MEC in this case? A possibility is that at densities where the TL (taken as stable) has a lattice parameter a between r_0 and r_1, the system segregates in two parts, both triangular lattices with lattice parameters r_0 and r_1. In terms of the external pressure P this would correspond to an isostructural transition[4] at some pressure. If an isostructural transition exists, it means that the energy as a function of the *volume* of the system has a region with negative second derivative. Since we are considering changes of volume that do not change the crystalline structure, we can derive this necessary condition for the existence of an isostructural transition easily from expression (1), and the result is

$$\sum_{\mathbf{r}_i \neq 0} \left[U''(r_i) - \frac{U'(r_i)}{r_i} \right] r_i^2 < 0. \qquad (6)$$

This condition is not satisfied by the hard-core plus linear-ramp potential. The conclusion is that in some range of pressures the TS is not the MEC of the system. The MEC for this potential, for different values of P and r_1/r_0 have been studied only recently,[5] and will be presented in the next section.

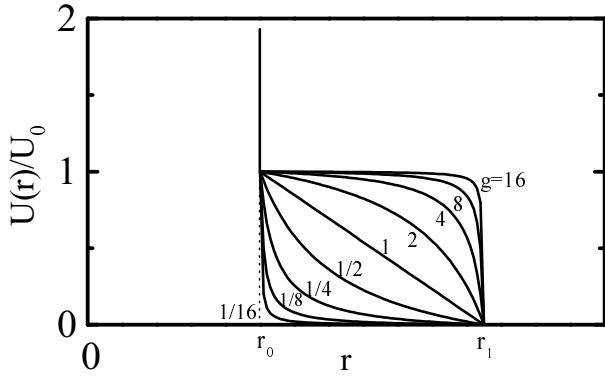## III. GROUND STATE FOR THE HARD-CORE PLUS SOFT REPULSIVE SHOULDER POTENTIAL

FIG. 2. The family of potentials $U_g(r)$.

Here I will present the MECs for a family of potentials that vanish beyond some distance r_1, are infinite for distances lower that some r_0, and in the intermediate range $r_0 < r < r_1$ are given by the expression

$$U_g(r) = U_0 \frac{g + \left[\left(\frac{r-r_0}{r_1-r_0} \right) (g - g^{-1}) - g \right]^{-1}}{g - g^{-1}}, \qquad (7)$$

which depends on the parameter g. When $g \to 1$ the potential reduces to a linear ramp between $U(r_0) = U_0$ and $U(r_1) = 0$. For $g \to \infty$ the potential has a square shoulder of height U_0 between r_0 and r_1, and for $g \to 0$ it reduces to the simple hard-core potential at $r = r_0$. The form of the potential for different values of g is shown in Fig. 2. This potential for particular values of g, and other related potentials have been studied since many years ago,[3,6] but usually with the idea of the isostructural transition in mind, and part of the richness of the model has been missed (however, see also [7]).
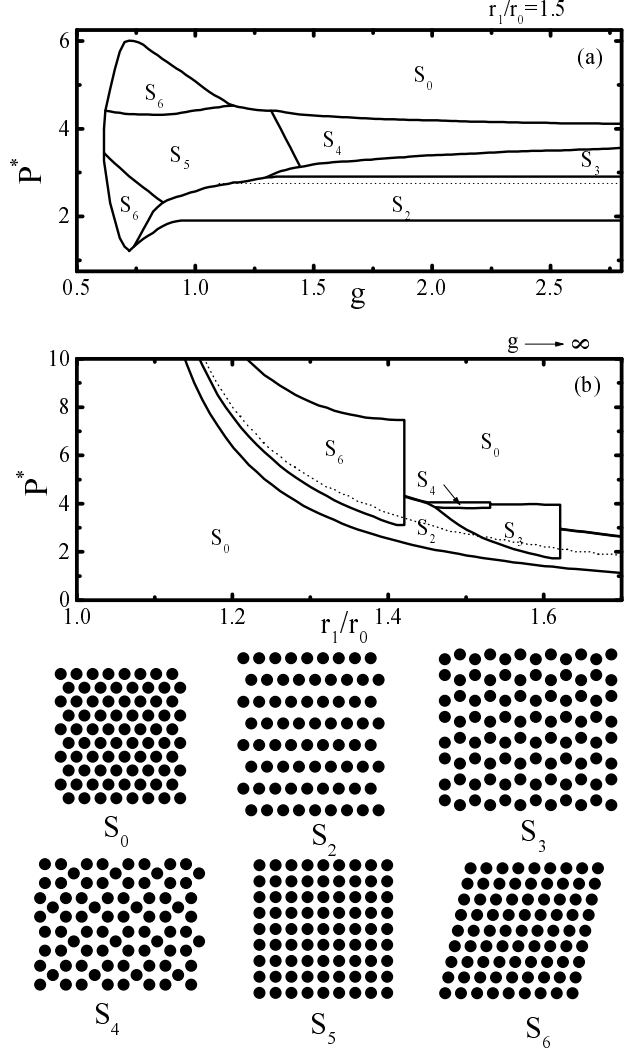

FIG. 3. Minimum energy configurations for particles interacting through the potentials $U_g(r)$, in the g-P^* plane for $r_1/r_0 = 1.5$ (a), and in the r_1/r_0-P^* plane for $g \to \infty$ (square shoulder potential)(b). Dotted lines would be the locations of isostructural transition between triangular lattices if other structures did not exist.

The MECs for a fixed value of $r_1/r_0 = 1.65$ as a function of g and P^*, and for a fixed value of $g \to \infty$ (square shoulder potential) as a function of r_1/r_0 and P^* are shown in Fig. 3 (the adimensional pressure P^* is defined as $P^* \equiv r_0^2 P/U_0$). The variety of configurations is intriguing, and some of them could be guessed only after doing some numerical simulations, annealing from high temperature configurations. Note that a direct transition between two TSs (one close packed, and the other expanded) is always preempted by the existence of additional lower energy structures. The structures in Fig. 3 were found by inspection, and they are the lowest energy configurations found within each region, but other (more stable) structures may have been missed. Note that some of the structures have more than one atom per unit cell

(2 for S_3 and 5 for S_4) and there may be unequivalent sites within the structure (2 for S_4).

It can be mentioned here the interesting fact that for potentials with a positive value of U_2 only at a discrete set of values of r, the compressibility of the system (at zero temperature) is zero, or the system is anisotropic (in the sense that second order tensors are not necessarily proportional to the identity). This is due to the above mentioned fact that stability of the structure requires the existence of particles at distances at which U_2 is positive. If the system is isotropic (symmetry C_3 or higher) an infinitesimal change in volume would make the number of particles at these distances be zero, and the structure destabilizes. So if the compressibility is different from zero, then the structure can have only a rotational symmetry C_2 (as it happens for instance with structure S_6 in Fig. 3), and the structure continuously deforms under changes of pressure, always keeping particles at distances where U_2 is positive.

IV. STABILITY AGAINST GLOBAL DEFORMATIONS: SCREENED CHARGES IN TWO DIMENSIONS

The stability against displacements of a single particle is by no means sufficient to guarantee the global stability of the TS. Let us consider another kind of perturbation of the TS, consisting in a rescaling of all x coordinates of the particles by a factor p, and all y coordinates by a factor p^{-1}, as illustrated in Fig. 4. This transformation preserves the volume per particle in the system so stability is achieved if the energy has a minimum around $p = 1$. For p very close to 1 we can take $p = 1 + \varepsilon$, with $\varepsilon \ll 1$, and do an expansion of the energy around $\varepsilon = 0$ up to second order. The result for the energy[8] is $E = E_0 + \widetilde{U}_2 \varepsilon^2/2$, with

$$\widetilde{U}_2 = \frac{1}{2} \sum_{\mathbf{r}_i \neq 0} \left[U''(r_i) + 3 \frac{U'(r_i)}{r_i} \right] r_i^2. \tag{8}$$

For potentials with $U'(r) < 0$, expression (8) may be negative even when (2) is positive.

For instance, for inverse power interactions $U(r) = U_0 (r/r_0)^{-\gamma}$, expression (8) takes the form

$$\widetilde{U}_2 = f_2(\gamma) U_0 (r_0/a)^\gamma \tag{9}$$

with

$$f_2(\gamma) = \frac{\gamma(\gamma - 2)}{2} \sum_{\mathbf{r}_i \neq 0} (r/a)^{-\gamma}, \tag{10}$$

which is only positive for $\gamma > 2$. For $\gamma < 2$ the negative sign of $\widetilde{U}_2$ would suggest that the TS is unstable. Note however, that $\gamma = 2$ coincides with the value below which $\widetilde{U}_2$ is dominated by long range interactions. In fact, for

$\gamma < 2$, expression (8) diverges, and a correct calculation of $\widetilde{U}_2$ should take into account a long distance cut-off of the interaction (or the existence of the edges of the system). The function $f_2(\gamma)$, which allows to calculate $\widetilde{U}_2$ using (9), is shown in Fig. 1. For $\gamma > 2$ it is calculated directly from expression (10). For $\gamma < 2$ it is calculated using (8), with an exponential cut-off in $U(r)$ of the form $\sim \exp(-r/r_0)$, with $r_0 \to \infty$. Note however, that the particular form of the cut-off does not influence the value obtained for $\widetilde{U}_2$. As we can see from the figure, for all γ the TS is stable. As for U_2, $\widetilde{U}_2$ vanishes when $\gamma \to 0$.
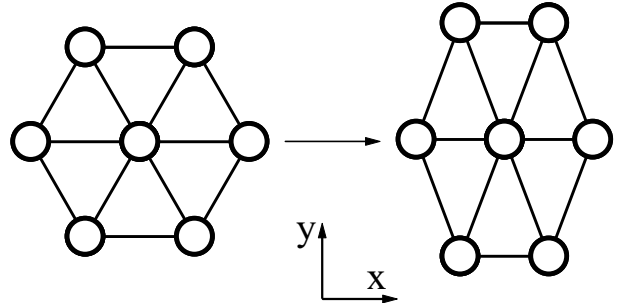

FIG. 4. Rescaling of the TS by a factor p along the x direction and p^{-1} in the y direction.

It is interesting to note that for $\gamma < 2$, the contribution to $\widetilde{U}_2$ from any particle is negative, only the existence of the cut-off makes the result to be positive. We can gain some insight on this point by a particular example. Let us take $\gamma = 1$, and a sharp cut-off at some distance r_0. To avoid the existence of sharp edges in the potential we shift the repulsive part so as to vanish at r_0, i.e, we will consider a potential of the form $U(r) = \theta(r_0 - r)(1/r - 1/r_0)$, and calculate the energy as a function of p for different values of r_0. We see (Fig. 5) that although $\partial^2 E/\partial p^2$ is always negative at $p = 1$, the interval around $p = 1$ with this characteristic narrows when r_0 increases, and in the limit of very large r_0, the value of $\partial^2 E/\partial p^2$ becomes positive at $p = 1$ as soon as we smooth the cut-off.
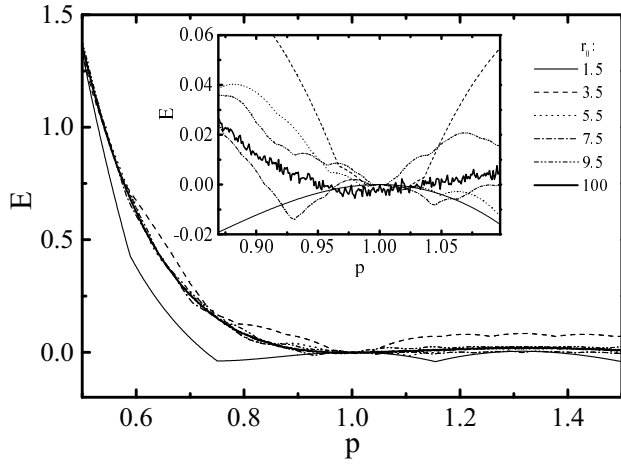
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FIG. 5. Energy per particle of the TS as a function of the rescaling parameter p, for particles interacting through a cut-off r^{-1} interaction, for different values of the cut-off r_0. The curves were vertically displaced to make them coincide in $p = 1$. Note in the inset that for all r_0 the value of $\partial^2 E/\partial p^2$ at $p = 1$ is negative, so the TS is unstable. However, the instability range rapidly diminishes with r_0.

The last example raises the following question: what is the minimum sharpness of the cut-off necessary to get a negative value of $\widetilde{U}_2$ for some range of values of the cut-off parameter r_0? For the family of potentials of the form $\exp\left[-(r/r_0)^\mu\right]/r^\gamma$, a numerical calculation based on (8) shows that for $\mu < 2$, $\widetilde{U}_2$ is positive for any r_0 and γ. For $\mu > 2$ and if γ is lower than some value $\gamma_0(\mu)$, there exists a range for r_0 such that $\widetilde{U}_2$ is negative. The function $\gamma_0(\mu)$ goes to zero when $\mu \to 2^+$, and increases with μ. It becomes 1 for μ slightly larger than 3. In all cases the instability region occurs when the cut-off parameter r_0 is close to the lattice parameter of the TS.

V. SUMMARY AND FURTHER DISCUSSIONS

It was shown in this paper that identical particles interacting through repulsive central forces in two dimensions may have a minimum energy configuration very different than the usually expected triangular structure. This may happen for interaction potentials as simple as the hard-core plus linear-ramp potential,[9] or for sharply cut off power law interactions of the form $\theta(r_0 - r)\, r^{-\gamma}$, if $\gamma < 2$.

We have concentrated here in the two-dimensional case. But it is not difficult to see that some of the conclusions can be extended to three dimensions. For instance, it is immediate to generalize expression (2) to three dimensions. The equivalent expression is[10]

$$U_2^{(3D)} = a^2 \sum_{\mathbf{r}_i \neq 0} \left[U''(r_i) + 2\frac{U'(r_i)}{r_i} \right]. \tag{11}$$

Also the necessary condition (6) for the existence of an isostructural transition can be generalized to:

$$\sum_{\mathbf{r}_i \neq 0} \left[U''(r_i) - 2\frac{U'(r_i)}{r_i} \right] r_i^2 < 0. \tag{12}$$

Expression (11) may be negative even if (12) is not satisfied. Again this happens, for instance, for the hard-core plus linear ramp-potential. In three dimensions the *a priori* expected structures for simple spherical potential are the high symmetry structures sc, bcc, fcc, or hcp. Are they the only MECs of this potential? The answer is negative. In Fig. 6 we see a *preliminary* diagram of MECs for this potential as a function of P^* (now defined as $P^* = r_0^3 P/U_0$) and r_1/r_0. This was obtained searching for the MEC among all crystalline systems with no more than two parameters determining their structure (this restriction was used only to facilitate the search). These are the cubic (including sc, bcc, and fcc Bravais lattices), tetragonal (simple (t) and body centered (bct)), rhombohedral (rh), and hexagonal systems. Only structures with one atom per unit cell were considered for simplicity, with the only exception of hexagonal structures (h), where the closed packed structure (hcp, with two atoms per unit cell) was included considering its well known stability.
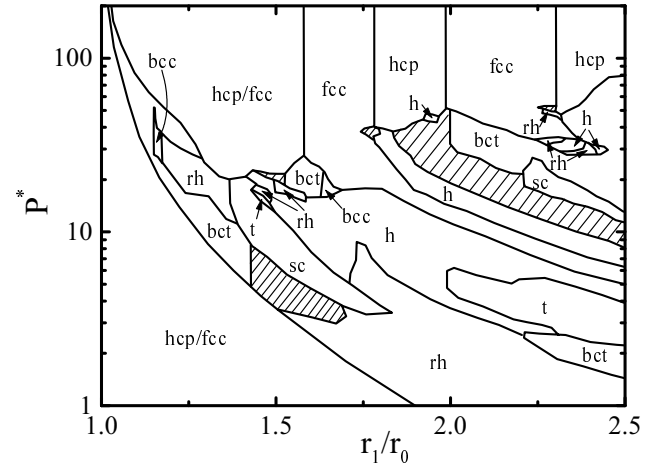

FIG. 6. MECs for the hard-core plus linear-ramp potential in three dimensions. The search was performed among structures of the cubic, tetragonal, rhombohedral, and hexagonal systems. Dashed regions are zones where none of these can be the MEC. See the text for more details.

The results of Fig. 6 show that almost all of these structures are the MEC among the considered ones in some region of the r_1/r_0-P^* plane. In addition, and having in mind the configurations found in the two dimensional case, it would not be surprising that other structures corresponding to lower symmetry crystalline systems, or structures with a more complex unit cells exist.

In connection with this, notice that the dashed regions in Fig. 6 correspond to lowest energy configurations (among the ones already mentioned) that have no particles at distances r_0 or r_1, and according to previous discussions we know that this structure cannot be stable, so the MEC is none of the considered ones. Clearly, numerical simulations are needed to exhaustively find all MECs for this or other related potentials.

Another point that was not touched upon in this paper is the problem of stability at finite temperatures. For the hard-core plus linear-ramp potential in two dimensions a detailed discussion has been given elsewhere.[5] I will only mention here the interesting fact that in some cases the melting of the crystalline structures is anomalous (in the sense that it occurs with an increasing in density) due to the sudden availability of configuration space at higher energies upon melting (which may be assimilated to an effective reduction of particle size at melting).

Other interesting issue concerns the dynamics of these structures. For instance, for the hard-core plus linear-ramp potential (at zero temperature), if we increase the external pressure smoothly, there is a value at which the TS would have a lattice parameter lower than r_1, and the structure destabilizes against displacement of single particles. Since particles in different positions will move in rather independent directions, we expect to obtain a disordered (metastable) structure at high pressures. For potentials such as the sharply cut off $1/r$, the instability is against deformations involving a large number of particles, and thus the metastable structures obtained by increasing pressure are expected to consist of large patches of particles, deformed along different directions. This is in fact what is obtained in numerical simulations. This phenomenon, as well as the appearance of metastable structures when decreasing the temperature from a finite value to zero[5] are important in connection with the transition to the glass state.

Although the kind of potentials needed to obtain the behaviors discussed in this work are difficult to find in atomic systems, it is reasonable to expect that they have physical realizations in colloidal dispersions,[11] where the interaction potential between particles can be changed a great extent through the applications of different techniques.

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[1] A. P. Smith, Phys. Rev. B **43**, 11 635 (1991); **42** 1189 (1990); A. P. Smith and N. W. Ashcroft, *ibid.* **38**, 12 942 (1988); A. R. Denton and J. Hafner, Phys. Rev. B **56**, 2469 (1997).

[2] For lattices with lower rotational symmetry than C_3, the cuadratic part of the potential is no longer isotropic, and in this case the negativeness of expression (2) is a *sufficient* condition for the instability of the structure against single particle displacements.

[3] P. C. Hemmer and G. Stell, Phys. Rev. Lett. **24**, 1284 (1970); Stell and P. C Hemmer, J. Chem. Phys. **56**, 4274 (1972).

[4] P. Bolhuis, M. Hagen, and D. Frenkel, Phys. Rev. E **50**, 4880 (1994); C. F. Tejero, A. Daanoun, H. N. W. Lekkerkerker, and M. Baus, Phys. Rev. E **51**, 558 (1995); P. G. Bolhuis and D. Frenkel, J. Phys. Cond. Matter **9**, 381 (1997).

[5] E. A. Jagla, Phys. Rev. E, in press (preprint cond-mat #9805059).

[6] J. M. Kincaid, G. Stell, and C. K. Hall, J. Chem. Phys. **65**,2161 (1976); J. M. Kincaid, G. Stell, and E. Goldmark, J. Chem. Phys. **65**, 2172 (1976); J. M. Kincaid and G. Stell, J. Chem. Phys. **67**, 420 (1977); J. M. Kincaid and G. Stell, Phys. Lett. **65A**, 131 (1978).

[7] C. Rascón, E. Velasco, L. Mederos, and G. Navascués, J. Chem. Phys. **106**, 6689 (1997); P. C. Hemmer, G. Stell, E. Velasco, L. Mederos, and G. Navascués, SUSB College of Engineering and Applied Sciences Report #758, April, 1998.

[8] In deriving (8), the fact that for the TS (symmetry C_6) all invariants up to fourth order in (x, y) are proportional to r was used. In the case of a lattice with symmetry C_4 (the square lattice) there is an additional fourth order invariant, namely x^2y^2, and in the corresponding expression for $\widetilde{U}_2$ there are terms proportional to $x_i^2 y_i^2 / r_i^2$.

[9] Although it was not discussed here, for particular values of the parameters this potential has as is sMEC the structure of a random quasicrystal (see [5]).

[10] This expression holds for all lattices that have its atoms in environments of cubic or higher symmetry. As in the two-dimensional case, for structures with lower symmetry negativeness of $U_2^{(3D)}$ as given by (11) is a *sufficient* condition for the instability of the structure.

[11] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1991), 2nd ed. W. C. K. Poon and P. N. Pusey, in *Observation, Prediction and Simulation of Phase Transitions in Complex Fluid,* edited by M. Baus, L. F. Rull, and L. P. Ryckaert (Kluwer Academic Publishers, Dordrecht, 1994), pp. 3-44; D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*, (Academin Press, London, 1983), ch. 6.